Electronic Supplementary Information

EXPERIMENTAL SECTION

Chemicals and materials

The ITO conductive electrode was gained from Zhuhai Kaivo Electronic Components Co. Ltd., China. PCT antigen (Ag), antibody (Ab) and bovine serum albumin (BSA) were purchased from Shanghai Aladdin Biochemical Technology Co. Ltd., (Shanghai, China). Stannous chloride ($SnCl_2 \cdot 2H_2O$), trisodium citrate ($Na_3C_6H_5O_7 \cdot 2H_2O$), mercaptoacetic acid, ferrous sulfate ($FeSO_4 \cdot 7H_2O$) were purchased from Tianjin Kermel Chemical Co. Ltd., (Tianjin, China). Polyvinyl pyrrolidone, Cadmium chloride ($CdCl_2 \cdot 2H_2O$), fullerene, sulfur and selenium powder were obtained from Sinopharm Chemical Reagent Co.Ltd., (Shanghai, China). All other reagents were of analytical grade and ultrapure water was used throughout the study.

Apparatus

All photoelectrochemical measurements were performed with an electrochemical workstation (Zahner Zennium PP211, Germany). The surface morphology of the sample was obtained from scanning electron microscopy (SEM, S-3400). Transmission electron micrographs (TEM) were measured on an H-800 microscope (Hitachi, Japan). X-ray photoelectron spectra (XPS) were elucidated using an ESCALAB 250 electron energy spectrometer (Thermo Fisher Scientific, USA) and the X-ray excitation source was monochromated Al Ka 150 W. UV-vis spectra were obtained on a Shimadzu UV-3101PC spectrometer (Japan). X-ray diffraction (XRD) patterns were obtained by using D8 focus diffractometer (Bruker AXS, Germany).

Preparation of flower-like Sn_3O_4

The preparation of Sn_3O_4 was carried out according to the previous reported method with some modifications.[1] Firstly, 5 mmol of $SnCl_2 \cdot 2H_2O$ (1.1282 g) and 12 mmol of trisodium citrate ($Na_3C_6H_5O_7 \cdot 2H_2O$, 3.5393 g) was co-dissolved into 12.5 mL of ultrapure water, the mixture was allowed stirring under room temperature, and the well-mixed solution as solution A. In the meantime, 0.3 g of NaOH was dissolved into 12.5 mL of ultrapure, and as solution B. Secondly, these two homogeneous solutions were mixed, and continued stirring for another 24 h at room atmosphere. After that, the mixture was transferred to a 50 mL Teflon-lined autoclave and maintained 180 °C for 12 h. Finally, the yellow product was washed with ultrapure water for 5 times, then dried at 60 °C.

Synthesis of FeS_2 nanoparticles

The synthesis of FeS_2 was processed via a hydrothermal method.[2] Briefly, 0.5881 g of $Na_3C_6H_5O_7 \cdot 2H_2O$ and 0.5000 g of polyvinyl pyrrolidone (PVP, K-24) were dispersed in 60 mL of ultrapure water under tempestuously stirring to form a pellucid solution. Then, 1.3911 g of $FeSO_4 \cdot 7H_2O$ was added into the solution, and made continues stirring for another 30 min. After that, 10 mL of NaOH (1.5 M) solution was added into the above solution drop by drop, followed by adding 0.4801 g of sulfur powder into the solution, and the mixture was allowed to stirring persistently until a homogeneous solution obtained. Then, the mixture was transferred in to a 100 mL Teflon-lined autoclave, maintaining 180 °C for 24 h. After the reaction, the product was washed with ultrapure water and ethanol, finally, dried at 60 °C.

Synthesis of C_{60} QDs

The synthesis of C_{60} QDs was according to a previous resport with some modified.[3] First, 5 mg of fullerene particles was added into 5 mL of toluene with violent stirring to obtain a purple homogeneous solution. Then, 5 mL of ultrapure water was added into the above solution and the resulted mixture was treated ultrasonically for about 24 h to thoroughly get rid of the toluene. Ultimately, the obtained buff fullerene dispersion was kept for further use.

Synthesis of CdSe nanoparticles

The praparation of CdSe was carried out through a previous reported method.[4] Firstly, the precursor NaHSe was prepared as follow: 0.0395 g of Se powder, and 0.0400g of $NaBH_4$ were dissolved in 2 mL ultrapure water under stirring until the mixture solution turned transparent. At the same time, 0.0384 g of $CdCl_2 \cdot 2H_2O$ was dissolved in 80 mL of ultrapure water, and 250 μL mercaptoacetic acid was added in the solution, the pH was adjusted to 9.0 by NaOH (1.0 M). Then, the as-prepared NaHSe solution was added into the above solution, and the mixture was stirred for another 2 h at room temperature. Finally, the product was purified by centrifugation with ethanol and dried.

Preparation of FeS_2-Ab_2 bioconjugates

3 mg of prepared FeS_2 was dispersed in 1 mL of PBS buffer solution (pH 7.4, 0.1 M), then, 20 μL of mixed crosslinking agent (5mg/mL of EDC and 1mg/mL of NHS) was added, and activated for 0.5 h at 37 °C. After that, 200 μL of Ab_2 (1 μg/mL) was added into the above solution, and incubated gently at 37 °C for 5 h. Finally, the mixture was centrifuged and washed with PBS (pH 7.4, 0.1 M), and as well dispersed

into 1 mL PBS buffer solution stored at 4 °C for later use.

The assembly of PEC sensor

For better detection, the ITO conductive electrode was first cut into suitable size (2 cm×0.8 cm), and been ultrasonic cleaning with acetone, ethanol, ultrapure water in turn. For modification, 10 μL of photosensitive materials of Sn_3O_4 (5 mg/mL), C_{60} QDs, and CdSe (5 mg/mL) were dropped onto the electrode successively, after dried naturally at room temperature, 6 μL of mixture (20 mg/mL of EDC and 10 mg/mL of NHS) and 4 μL of standard PCT antigen was decorated on to the photoactive electrode, the electrode was incubated for 1 h. After washed the dried electrode, and blocked the non-specific sites with BSA (1%), the electrode was incubated with 6 μL mixture (1μg/mL of Ab_1 and various concentration of target PCT) for 40 min at room temperature. Finally, 6 μL of FeS_2-Ab_2 was modified onto the electrode and allowed naturally dried for PEC measurement.

PEC measurements

The finished PEC electrode as work electrode was dipped into 10 mL of PBS buffer solution containing with 0.1 M of ascorbic acid (AA), performing on an photoelectrochemical workstation and adopted three-electrode configuration (saturated calomel electrode (SCE) for reference, platinum electrode for counter) for measuring the PEC response through standardized recycling method, and the 100 W LED lamp (white light, 400-700 nm) is used as the stimulation resource.

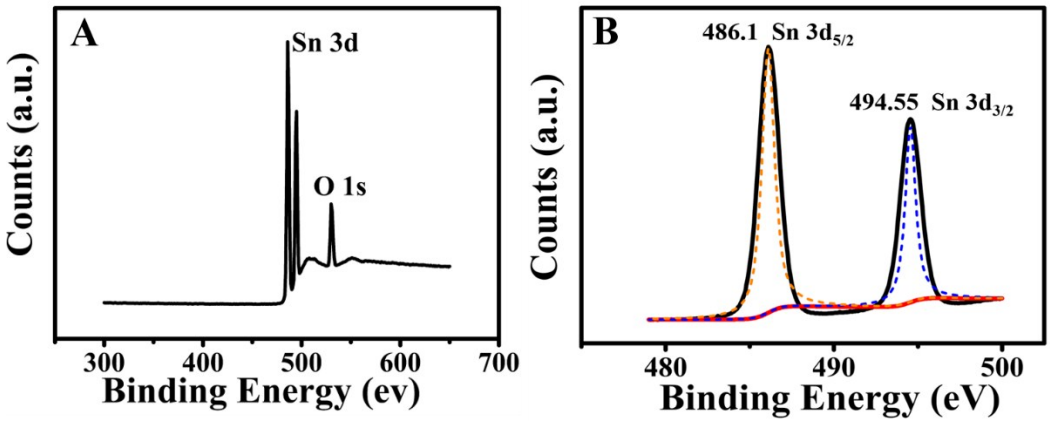

Figure S1. The XPS peak of (A) Sn_3O_4 and (B) Sn element.

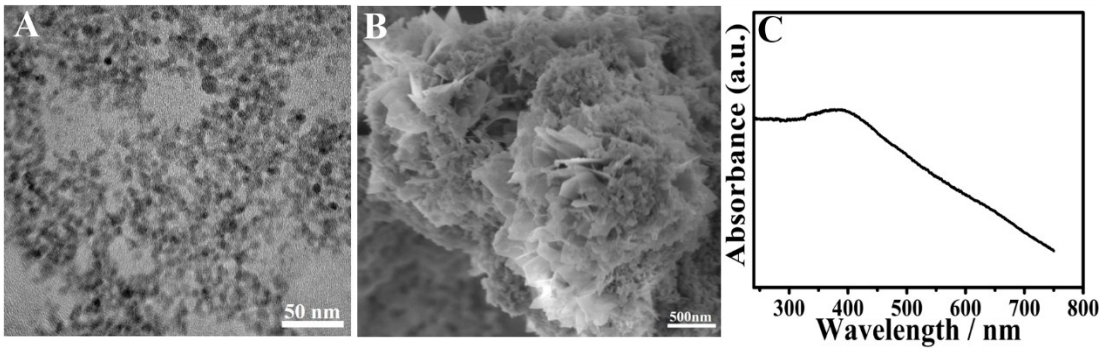

Figure S2. The TEM image of CdSe (A), the SEM image of Sn_3O_4/C_{60}/CdSe (B), and the UV-Vis absorption spectrum of FeS_2 nanoparticles.

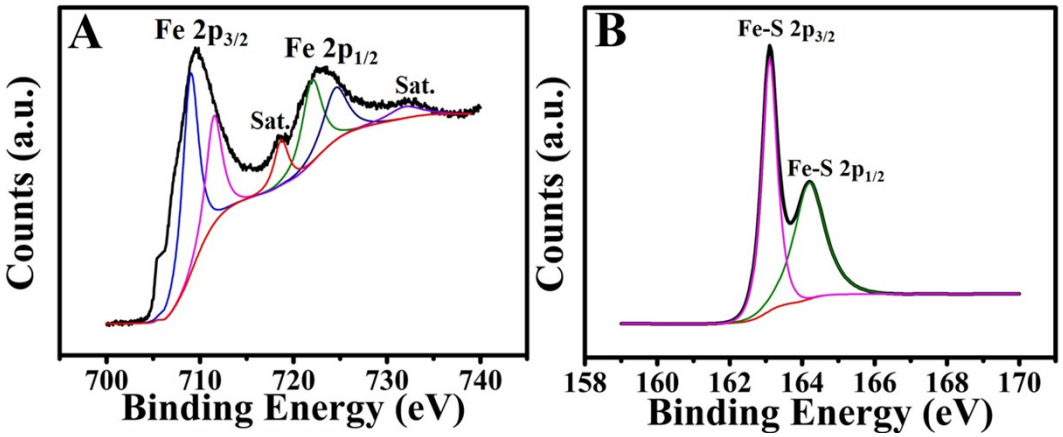

Figure S3. The XPS peaks of (A) Fe element and (B) S element of FeS_2 nanoparticles.

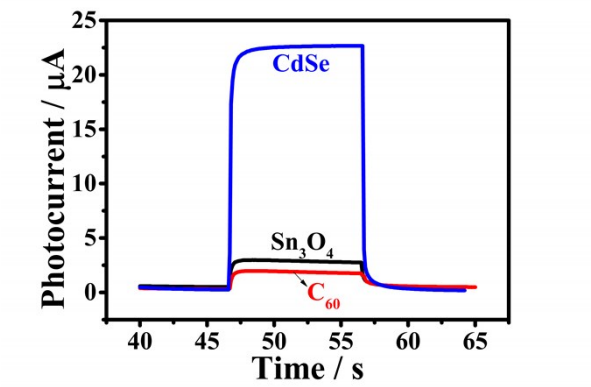

Figure S4. The photocurrent of pure Sn_3O_4, pure C_{60}, and pure CdSe.

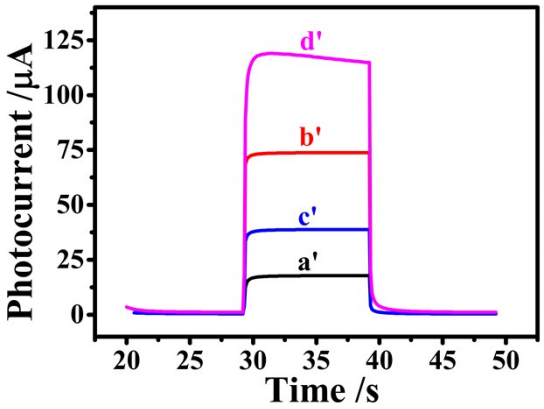

Figure S5. The comparation of PEC response for different electrode. (a') Sn_3O_4/C_{60}, (b') Sn_3O_4/CdSe, (c') C_{60}/CdSe, and (d') Sn_3O_4/C_{60}/CdSe.

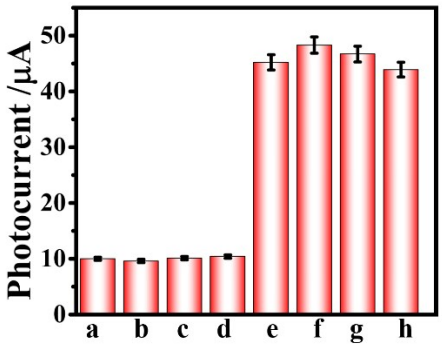

Figure S6. The selectivity of the sensor. Photocurrents response of ITO/Sn_3O_4/C_{60}/CdSe/EDC-NHS/Ag/BSA/(Ab_1+terget Ag)/Ab_2-FeS_2 to the interfering substances (0.5 ng/mL) exist alone and coexistence with PCT (0.005 ng/mL): (a) Blank, (b) blank+ Aβ, (c) blank+ BNP, (d) blank+ PSA, (e) PCT, (f) PCT+ Aβ, (g) PCT+ BNP, (h) PCT+PSA.

Table S1. The developed PEC sensors for detecting procalcitonin compared to other published immunosensor.

Method	Linear range (ng/mL)	Detection limit (fg/mL)	Reference
Electrochemical sensor	0.0018 - 500	360	Shen et al.[5]
Electrochemical sensor	0.001-20	430	Liu et al.[6]
Electrochemiluminescence sensor	0.1-50	41	Yang et al.[7]
Chemiluminescence sensor	0.0025-80	500	Nie et al.[8]
Photoelectrochemical sensor	0.05-100	17.3	Feng et al.[9]
Fluorescence sensor	0.1-10	250000	Zhou et al.[10]
This work	0.00001-10	3.5	This work

Table S2. Recovery results of PCT in human serum samples detected by the proposed PEC sensor (n=5)

sample (ng/mL)	Target added (ng/mL)	Average (ng/mL)	RSD (%)	Recovery (%)
0.56	0.005	0.5652	2.67	104
	0.5	1.073	3.49	102.6
	5.00	5.501	4.01	98.82

Reference

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